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Effect of the precursors on the deposition of (Ba, Sr)TiO₃ films

J.-H. Lee, W.-Y. Yang, S.-W. Rhee and D. Kim¹

Electrical and Computer Engineering Division, Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea

¹ *Microelectronics Lab., Samsung Advanced Institute of Technology, San #24, Nongseo-ri, Kiheung-Eup, Yongin-City, Kyungki-Do 449-900, Korea*

Abstract: Ba and Sr precursors for (Ba,Sr)TiO₃ films have been studied including (1) M(tmhd)₂-Lewis base adduct (M = Ba or Sr, tmhd = tetramethylheptanedionate), (2) M(ketoester)₂, (3) M(diester)₂, and (4) M(methd)₂ (methd = methoxyethoxytetramethyl-heptanedionate). In case of ketoester and diester ligands, premature dissociation of the ligand was observed while M(methd)₂ shows good volatility and stability. Boiling point of Lewis base has a strong effect on the volatility of M(tmhd)₂-Lewis base. Most of the Ti precursors were easily evaporated at low temperatures and thermal stability of Ti precursors could be controlled with diketone and alkoxide ligands. Ti(mpd)(tmhd)₂ (mpd = methyl-pentanediol) shows higher thermal stability than Ti(i-OPr)₂(tmhd)₂ or Ti(dmae)₄ (dmae = dimethylaminoethoxide). To characterize the deposition behavior, (Ba,Sr)TiO₃ films were deposited at the deposition temperature of 400 ~ 480°C using a direct liquid injection method. Composition uniformity and step coverage were largely affected by Ti precursors.

1. INTRODUCTION

Dynamic random access memory (DRAM) density has been increased steadily but each successive generation has maintained equal charge storage within continually shrinking cell areas. New materials that display high dielectric constant such as (Ba,Sr)TiO₃ [BST] are promising candidate for this application [1-3]. High dielectric constant of BST film (>200), compared to Ta₂O₅ (20 ~ 25) or SiO₂/SiN bi-layer, is due to its perovskite crystal structure, in which a large dipole moment is induced when the electric field is applied. BST film offers a unique combination of high dielectric constant, low dc leakage, low dispersion at high frequencies, and high temperature operation. Recently, progress has been realized using liquid delivery metal-organic chemical vapor deposition (MOCVD) of BST film for advanced DRAM applications [4-8].

The physical and chemical properties of the precursors used for MOCVD film growth are critical. Numerous Ba and Sr precursors have been studied including M(tmhd)₂-Lewis base system (M = Ba or Sr, tmhd = tetramethylheptanedionate)[9,10]. For efficient flash vaporization during liquid delivery, precursor decomposition and ligand exchange between metal precursors must be avoided. Chemical modification of the precursor molecule can be used to enhance the precursor transport and volatility [11-13]. The characteristics of precursors and their effects on the properties of (Ba,Sr)TiO₃ films have not been clearly identified. Also, most of the researchers have deposited BST films at the deposition temperature higher than 500°C to obtain good electrical properties without post-annealing process. However, in order to prevent bottom electrode-Si reactions and oxidation of bottom electrode, and to obtain good step-coverage, it is essential to deposit BST films at lower temperatures.

In this study, thermal stability, vaporization, and decomposition behavior of Ba, Sr, and Ti precursors were evaluated including M(tmhd)₂-Lewis base system (M = Ba or Sr, tmhd =

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tetramethylheptanedionate), $M(\text{ketoester})_2$, $M(\text{diester})_2$, and $M(\text{methd})_2$ (methd = methoxyethoxytetramethylheptanedionate) for Ba and Sr and $\text{Ti}(\text{mpd})(\text{tmhd})_2$ (mpd = methypentandiol), $\text{Ti}(\text{i-OPr})_2(\text{tmhd})_2$, $\text{Ti}(\text{dmae})_4$ (dmae = dimethylaminoethoxide) for Ti. To characterize the deposition behavior, (Ba,Sr) TiO_3 films were deposited at the deposition temperature of 400 ~ 480°C using a direct liquid injection method. Composition uniformity and step coverage were also studied.

2. EXPERIMENTAL

Fig.1 and 2 show ligand structure for Ba, Sr and Ti precursors. Thermal stability and volatility of Ba, Sr, and Ti precursors were analyzed by thermogravimetry (TGA) and differential scanning calorimeter (DSC) under 10°C/min heating rate in Ar atmosphere.

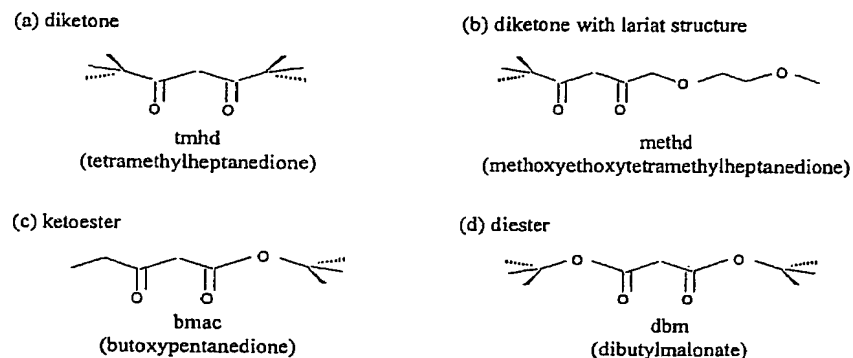


Fig.1 Chemical structure of the ligands for Ba and Sr precursors

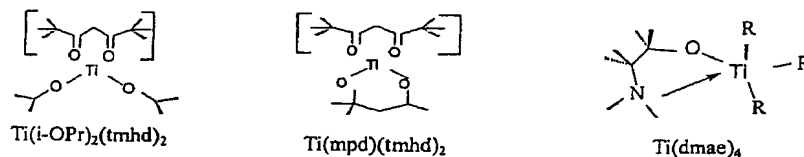


Fig.2 Chemical structure of the Ti precursors

The vaporized species were analyzed by mass spectrometer at the vaporization temperature of 200°C. A single cocktail solution of Ba, Sr, and Ti precursors were used for MOCVD of BST films. The schematic diagram of the reactor was shown elsewhere [10, 12]. The single cocktail

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source was pressurized by Ar and metered through LMFC (Liquid Mass Flow Controller) and flash-vaporized in the vaporizer. The vaporized source was fed into the reactor through the heated showerhead and delivered finally onto the heated substrate. Composition of the film was determined by X-ray fluorescence (XRF) and surface morphology was observed using scanning electron microscopy.

3. RESULTS AND DISCUSSION

3.1 chemical and physical properties of precursors

Among various diketone compounds of Ba and Sr, by far the tmhd ligand is most popular. Molecules with alkaline earth metals such as Ba and Sr are notorious for their low volatility due to the aggregation. To reduce the aggregation and obtain high volatility, spatial shielding of $\text{Ba}(\text{tmhd})_2$ or $\text{Sr}(\text{tmhd})_2$ by reducing the electrostatic binding force with polyether as a Lewis base was studied by Gardiner et al. [14]. Fig. 3 shows the molecular structure of the Lewis base so far tried including polyamines.

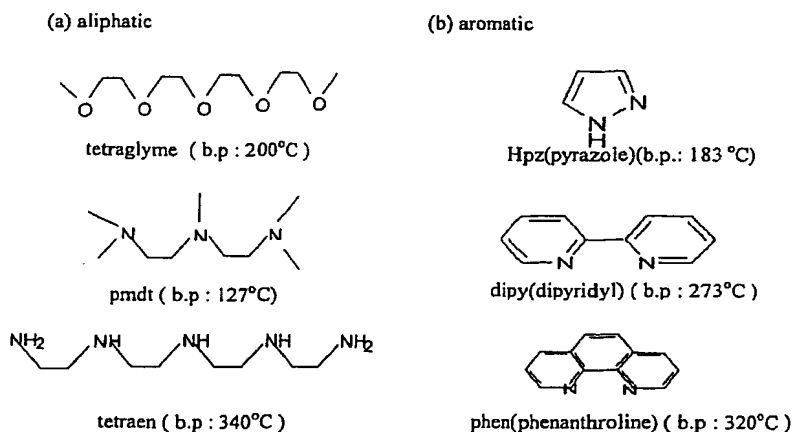


Fig. 3 Chemical structure of Lewis base to form $M(\text{tmhd})$ -Lewis base adducts

To prevent the aggregation, ketoester and diester ligands with oxygen was developed, which can satisfy large coordination number of Ba and Sr metals. In addition to ketoester, bmac (butoxypentanedione) shown in Fig. 1(c), diester ligands such as dbm (dibutylmalonate), en (1,3-di(di-ethoxy)propanedione), men (1,3-di(methoxydiethoxy) propanedione), ep (ep = 1,3-di(di-ethoxy) propanedione) and meen (1,3-di(methoxy)-2-methoxydiethoxyethylpropanedione) were tried. TGA/DSC analysis of Sr precursor with diester ligand, ep, showed weight loss with exothermic reaction at the temperature range of 180 ~ 280°C. The residue above 30% was observed

at 500°C. Mass spectra of $\text{Sr}(\text{ep})_2$ evaporated at 200°C showed only mass ion species without metal through the overall detection time. Similar TGA/DSC patterns and mass spectra were observed in other $\text{Sr}(\text{L})_2$ (L = diester or ketoester) systems. In ketoester and diester ligands, chemical bonding between alkoxy group and diketone is weak and premature dissociation occurred to give the evaporation of alkoxy group and agglomeration of remaining species. Similar results were observed in $\text{Ba}(\text{L})_2$ system.

$\text{M}(\text{tmhd})$ -Lewis base adducts have been most popular and it is believed that the properties of the adduct strongly depends on the properties of the Lewis base, especially the boiling point. The Lewis base, Hpz (b.p : 186°C), bipy (b.p : 273°C), and phen (b.p : 320°C) (Hpz = pyrazole, bipy = bipyridyl, phen = phenanthroline) were selected for the adduct formation with $\text{M}(\text{tmhd})_2$ (M = Ba or Sr). As shown in Fig. 4, TGA patterns of Hpz and bipy have shoulders around 190°C and 220°C, respectively. However, no shoulder was observed when using phen. Also, the vaporization temperature and final residue of $\text{Sr}(\text{tmhd})_2$ -phen₂ were lower than that of hpz and bipy.

Mass spectra of $\text{Sr}(\text{tmhd})_2$ using bipy and phen as a Lewis base were obtained and in case of bipy, dissociated Lewis base was detected at early detection time. And then, aggregated species of Sr precursors were detected. Similar results were obtained with bipy. However, no aggregated species of Ba and Sr precursors was detected with phen.

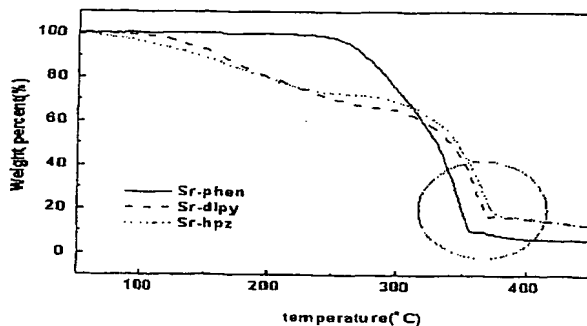


Fig. 4 TGA patterns of $\text{Sr}(\text{tmhd})_2$ -Lewis base systems in Ar atmosphere

This may be caused by the fact that Lewis base with low boiling point was easily dissociated and then coordinatively unsaturated $\text{Sr}(\text{tmhd})_2$ was aggregated. However, in case of phen, neither aggregation nor dissociation was occurred due to its high boiling point. The dissociation temperature of the $\text{M}(\text{tmhd})$ and Lewis base was shown to be a little higher than the boiling point of the Lewis base itself [4].

Mass signals of the gas species from $\text{Ba}(\text{methd})_2$ under the isothermal condition of 200°C after 120s were obtained. Mass-to-charge ratio (m/z) 395 and 995, which can be assigned to $+\text{Ba}(\text{methd})$ and $+\text{Ba}_2(\text{methd})_3$ were detected. These peaks represent the monomeric and dimeric species, respectively. Compared to mass signals of the gas species from $\text{Ba}(\text{tmhd})_2$ at the same condition, $\text{Ba}(\text{methd})_2$ shows smaller peak intensity of dimeric species and no trimeric species, which means

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that spatial shielding of Ba and Sr metals are achieved by modifying tmhd ligand with methoxy and ethoxy groups. Similar results were obtained with $\text{Sr}(\text{methd})_2$ precursors.

3.2 MOCVD OF BST FILMS

Fig. 5 shows the variations of film composition, $\text{Ba}/(\text{Ba}+\text{Sr})$ cation ratio versus the deposition temperature (T_s). It was already published that $\text{Ba}/(\text{Ba}+\text{Sr})$ ratio was almost constant over the deposition temperature range above 420°C with $\text{M}(\text{tmhd})$ -Lewis base adduct system [4, 10]. But with $\text{M}(\text{methd})$ system, the incorporation rate of Ba is relatively lower than Sr, which is believed to be the stronger shielding effect of oxygen in the side chain on Ba. For that reason, the concentration of Ba and Sr in the film is more temperature sensitive.

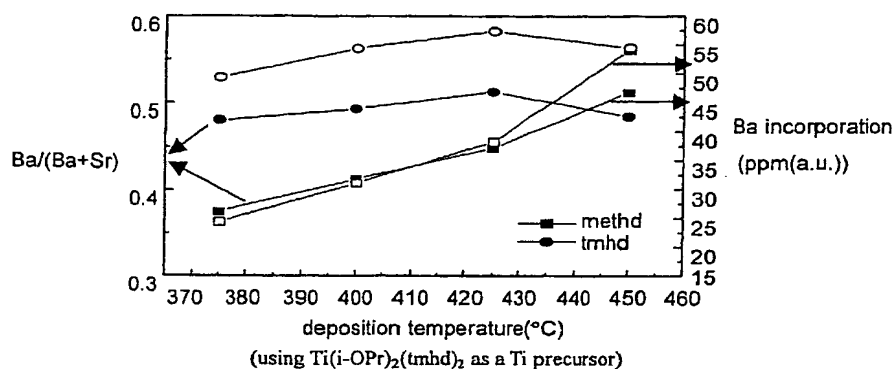


Fig. 5 Variation of film composition, $\text{Ba}/(\text{Ba}+\text{Sr})$ cation ratio, versus the deposition temperature (T_s) and the incorporation rate of Ba into the film (Ba:Sr feed ratio = 1:1).

Fig. 6 shows the variation of film composition, $\text{Ti}/(\text{Ti}+\text{Ba}+\text{Sr})$ cation versus the deposition

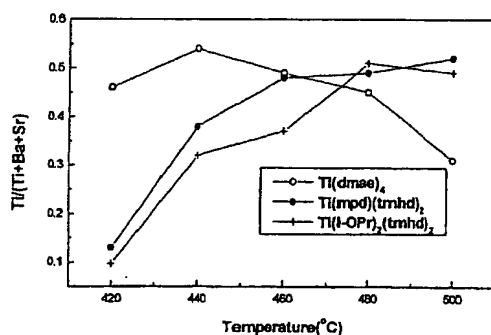


Fig. 6 Ti incorporation as a function of the deposition temperature using $\text{Ti}(\text{dmae})_4$.

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$\text{Ti}(\text{i-OPr})_2(\text{tmhd})_2$ and $\text{Ti}(\text{mpd})(\text{tmhd})_2$ as a Ti precursor

temperature (T_s) with various Ti sources. Ti cation incorporation behavior was largely dependent on the Ti precursor and deposition temperature. Ti incorporation behavior of $\text{Ti}(\text{mpd})(\text{tmhd})_2$ was similar to that of $\text{Ti}(\text{i-OPr})_2(\text{tmhd})_2$. Ti/(Ti+Ba+Sr) ratio was increased and then saturated above 500°C with $\text{Ti}(\text{mpd})(\text{tmhd})_2$, and above 460°C with $\text{Ti}(\text{i-OPr})_2(\text{tmhd})_2$. Below this temperature, surface reaction determines the deposition rate. With $\text{Ti}(\text{dmae})_4$, Ti incorporation was substantially higher and almost constant at the deposition temperature of 400 ~ 460°C. Ti-dmae bond is relatively weaker than Ti-tmhd bond. TGA/DSC experiment was performed for each precursor under Ar atmosphere.

$\text{Ti}(\text{i-OPr})_2(\text{tmhd})_2$ shows one endothermic peak at 176°C which represents the melting of the precursor. It also shows one endothermic peak at 208°C and an exothermic peak at 391°C. The peak at 208°C and 391°C represented the vaporization and decomposition of the precursor, respectively. On the other hand, $\text{Ti}(\text{mpd})(\text{tmhd})_2$ showed single exothermic peak at 281°C due to the evaporation and the final residue was below 3%. This results shows that the vaporization characteristics and thermal stability of $\text{Ti}(\text{mpd})(\text{tmhd})_2$ are better than that of $\text{Ti}(\text{i-OPr})_2(\text{tmhd})_2$. In case of $\text{Ti}(\text{dmae})_4$, only one single endothermic peak at 240°C appeared which was lower than $\text{Ti}(\text{mpd})(\text{tmhd})_2$. Fig. 7 shows DSC curves of Ti precursors in flowing oxygen. With $\text{Ti}(\text{i-OPr})_2(\text{tmhd})_2$, DSC curve exhibited two exothermic peaks at 290°C and 380°C. The peak at 290°C and 380°C represented the decomposition of i-OPr ligand and tmhd ligand, respectively.

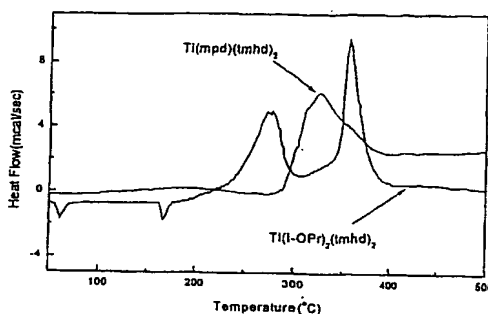


Fig. 7 DSC curves of $\text{Ti}(\text{mpd})(\text{tmhd})_2$ and $\text{Ti}(\text{i-OPr})_2(\text{tmhd})_2$ in O_2 atmosphere

In contrary to $\text{Ti}(\text{i-OPr})_2(\text{tmhd})_2$, $\text{Ti}(\text{mpd})(\text{tmhd})_2$ showed single exothermic peak at 350°C, indicating that the decomposition of mpd and tmhd ligands occurred nearly at the same temperature. $\text{Ti}(\text{dmae})_4$ showed also single exothermic peak at 275°C[6]. Based on TGA/DSC results, weak Ti-dmae bond strength makes Ti cation incorporation of $\text{Ti}(\text{dmae})_4$ more efficient than that of $\text{Ti}(\text{i-OPr})_2(\text{tmhd})_2$ or $\text{Ti}(\text{mpd})(\text{tmhd})_2$.

To investigate the effect of Ti precursors on the morphology of BST thin films, scanning electron microscope was used to observe films deposited on platinum node. As shown in Fig. 8, no

hump and protrusion were detected when BST thin films were deposited at the deposition temperature of 400 ~ 480°C with $\text{Ti}(\text{mpd})(\text{tmhd})_2$ and with $\text{Ti}(\text{dmae})_4$ [6]. However, humps as large as 200nm were detected with $\text{Ti}(\text{i-OPr})_2(\text{tmhd})_2$ above the T_s of 460°C.

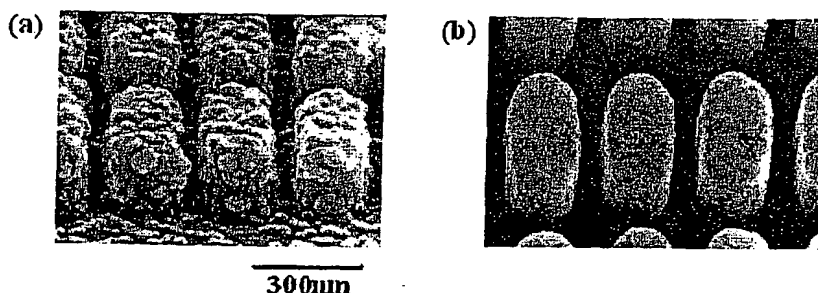


Fig. 8 SEM photographs of BST thin films deposited on Pt node at the deposition temperature of 460°C using (a) $\text{Ti}(\text{i-OPr})_2(\text{tmhd})_2$ and (b) $\text{Ti}(\text{mpd})(\text{tmhd})_2$ as a Ti precursor

Based on the above results, it is believed that $\text{Ti}(\text{i-OPr})$ bond was easily decomposed in the gas phase, and then agglomeration of Ti precursors occurred. The adsorption of agglomerated Ti species on the surface lead to the formation of Ti-rich hump[6]. Ti-rich hump region was alleviated by substituting $\text{Ti}(\text{i-OPr})$ weak bond with $\text{Ti}(\text{mpd})$ bond, or $\text{Ti}(\text{tmhd})$ strong bond with $\text{Ti}(\text{dmae})$ bond.

It is well known from the previous work that the stoichiometric or near stoichiometric composition gives better electrical properties and a deposition where the deposition rate was controlled by the surface reaction gives better step-coverage. A temperature was chosen in the surface controlled region that gives stoichiometric composition and step-coverage along with electrical properties was evaluated. Fig. 8 shows BST films using $\text{Ti}(\text{mpd})(\text{tmhd})_2$ as a Ti precursor is conformal.

The cation ratio of $\text{Ti}/(\text{Ti}+\text{Ba}+\text{Sr})$ inside the trench was measured using correlated EDX. Using $\text{Ti}(\text{mpd})(\text{tmhd})_2$, the Ti incorporation at the bottom of the trench was substantially higher than at the top of the trench. This non-uniformity was caused by the Ti-rich feed rate and different rate controlling mechanism on the top and bottom of the trench. With $\text{Ti}(\text{dmae})_4$, this non-uniform cation distribution could be alleviated [15].

4. CONCLUSIONS

In this study, Ba, Sr, and Ti precursors for MOCVD of BST films have been developed and their validity as a precursor was evaluated. In case of ketoester and diester ligands for Ba and Sr precursors, non-volatility was found due to the easy decomposition of ligand molecules. Boiling point of a Lewis base has an important effect on the volatility of $\text{M}(\text{tmhd})_2$ -Lewis base system. Among developed Ba and Sr precursors, $\text{M}(\text{methd})_2$ shows the best volatility. Contrary to Ba and Sr precursors, most of developed Ti precursors were easily sublimated at low temperatures. Thermal

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stability of Ti precursors could be controlled by properly selecting diketone and alkoxide ligands. $\text{Ti}(\text{mpd})(\text{tmhd})_2$ (mpd = methypentanediol) shows higher thermal stability than $\text{Ti}(\text{i-OPr})_2(\text{tmhd})_2$ or $\text{Ti}(\text{dmae})_4$ (dmae = dimethylaminoethoxide). To characterize the deposition behavior, $(\text{Ba,Sr})\text{TiO}_3$ films were deposited at the deposition temperature of $400 \sim 480^\circ\text{C}$ using a direct liquid injection method. Some Ti-rich hump and haziness of BST films, which was originated from gas phase reaction of $\text{Ti}(\text{i-OPr})_2(\text{tmhd})_2$ was alleviated with $\text{Ti}(\text{mpd})(\text{tmhd})_2$ or $\text{Ti}(\text{dmae})_4$. Step-coverage of $(\text{Ba,Sr})\text{TiO}_3$ films was largely affected by Ti precursors. With $\text{Ti}(\text{mpd})(\text{tmhd})_2$ as a Ti precursor, step-coverage was above 80% at the deposition temperature of 440°C . However, non-uniform $\text{Ti}/(\text{Ba}+\text{Sr}+\text{Ti})$ ratio was detected inside the trench. This non-uniformity was originated from different decomposition behaviors of Ba, Sr, and Ti precursors, and could be alleviated with $\text{Ti}(\text{dmae})_4$.

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